tetralin makes it seem probable that the cyclodehydration of aralkanols to polynuclear hydrocarbons proceeds through intermediate formation of the aralkene with subsequent isomerization (cyclization) of the latter.

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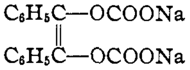
[CONTRIBUTION FROM THE CHEMISTRY LABORATORY OF THE UNIVERSITY OF MICHIGAN]

The Preparation and Reactions of Benzil-disodium

BY W. E. BACHMANN

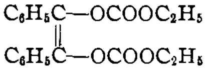
Beckmann and Paul[1] found that only one atom of sodium reacted with a molecule of benzil, $C_6H_5COCOC_6H_5$, and gave a violet colored solid; Nef[2] obtained the same product and considered that it was a molecular complex formed from a molecule each of benzil and benzil-disodium while Schlenk and Thal[3] believed it was a free radical. Staudinger and Binkert[4] were able to obtain benzil-dipotassium by heating a benzene solution of benzil with metallic potassium. We have now found a convenient method for preparing benzil-disodium, $C_6H_5C(ONa){=}(NaO)CC_6H_5$, which has not been obtained previously; the disodium compound is formed by interaction of benzil and 2% sodium amalgam at room temperature in a mixture of ether and benzene. During the reaction the violet colored complex is formed as an intermediate and then gives way to the orange colored crystals of the disodium derivative. In like manner anisil, 4,4′-diphenylbenzil and α-naphthil are converted to the disodium derivatives by the action of sodium amalgam; anisil gives a violet complex corresponding to addition of one atom of sodium and then a yellow disodium derivative; 4,4′-diphenylbenzil gives a blue intermediate and then a brown-red compound; the intermediate compound obtained from α-naphthil is red-brown while the disodium derivative is red.

Benzil-disodium reacts readily with a number of reagents. Like the benzil-dipotassium compound of Staudinger and Binkert and the iodomagnesium compound of Gomberg and Bachmann,[5] benzil-disodium gives benzoin when it is treated with water and in practically quantitative yield; anisoin, 4,4′-diphenylbenzoin and α-naphthoin are obtained by hydrolysis of the disodium derivatives of the corresponding benzils. Oxygen of the air oxidizes benzil-disodium at room temperature; hydrolysis of the product gives benzoic acid and some benzilic acid. Although Beckmann and Paul reported that the violet complex of benzil-disodium and benzil did not react with carbon dioxide, we have found that carbon dioxide is readily absorbed by benzil-disodium; in the reaction apparently the sodium salt of stilbenedicarbonic acid (I) is formed; when treated with water the salt is decomposed with loss of carbon dioxide and benzoin is formed. The stable diethyl ester (II) of this acid is obtained by interaction of benzil-disodium and chloroethylcarbonate. This ester is readily hydrolyzed to benzoin by dilute alkali.



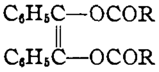
$$\begin{array}{l} C_6H_5C-OCOONa \\ \| \\ C_6H_5C-OCOONa \end{array}$$

I



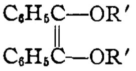
$$\begin{array}{l} C_6H_5C-OCOOC_2H_5 \\ \| \\ C_6H_5C-OCOOC_2H_5 \end{array}$$

II



$$\begin{array}{l} C_6H_5C-OCOR \\ \| \\ C_6H_5C-OCOR \end{array}$$

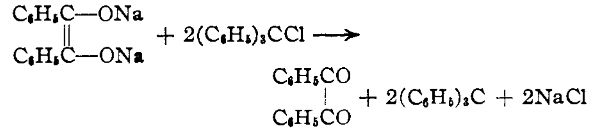
III



$$\begin{array}{l} C_6H_5C-OR' \\ \| \\ C_6H_5C-OR' \end{array}$$

IV

Esters of dihydroxystilbene are formed by treatment of the benzil-disodium with acid chlorides or anhydrides; with acetic anhydride stilbenediacetate (III, $R = CH_3$) is formed; benzoyl chloride gives stilbenedibenzoate (III, $R = C_6H_5$) and *p*-toluyl chloride yields stilbene-di-*p*-toluate (III, $R = C_6H_4CH_3$-*p*). Ethers are obtained by interaction of the disodium compound with alkyl halides; in this respect the disodium compound is more reactive than the iodomagnesium derivative. Methyl iodide gives stilbenedimethyl ether (IV, $R' = CH_3$), while allyl bromide yields stilbenediallyl ether (IV, $R' = CH_2CH{=}CH_2$). Triphenylchloromethane reacts rapidly with benzil-disodium but does not give an ether; instead benzil and triphenylmethyl are formed. In a



$$\begin{array}{l} C_6H_5C-ONa \\ \| \\ C_6H_5C-ONa \end{array} + 2(C_6H_5)_3CCl \longrightarrow \begin{array}{l} C_6H_5CO \\ | \\ C_6H_5CO \end{array} + 2(C_6H_5)_3C + 2NaCl$$

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[1] Beckmann and Paul, *Ann.*, **266**, 1 (1891).

[2] Nef, *ibid.*, **308**, 287 (1899).

[3] Schlenk and Thal, *Ber.*, **46**, 2850 (1913).

[4] Staudinger and Binkert, *Helv. Chim. Acta*, **5**, 703 (1922).

[5] Gomberg and Bachmann, THIS JOURNAL, **49**, 2584 (1927).

similar fashion iodine and sulfur react rapidly with benzil-disodium, removing the sodium atoms and giving benzil nearly quantitatively in addition to sodium iodide and sodium sulfide, respectively.

Benzaldehyde is converted nearly quantitatively to benzyl benzoate when allowed to stand with benzil-disodium at room temperature.

There is a similarity between the sodium derivative of benzil and the sodium derivative of aromatic ketones; both classes react readily with water, with iodine, with oxygen and with other reagents; moreover, while the sodium compounds are deeply colored, the esters, ethers and hydrogen derivatives are colorless. Although the monosodium derivatives of ketones add a second sodium atom when they are treated with 40% sodium amalgam, it was found that benzil-di-sodium does not react further with the stronger amalgam; when benzil is treated with excess of 40% sodium amalgam, benzil-disodium is formed.

TABLE I

REACTIONS OF BENZIL-DISODIUM

Weight of benzil taken, 3.0 g.

Reagent added Name	G.	Time for reaction	Product	Yield g.	Yield %	Solv. for recryst.	Cryst. form	M. p., °C.	Analyses, % Calcd. C	Analyses, % Calcd. H	Analyses, % Found C	Analyses, % Found H
Water	Exc.	1 min.	Benzoin[a]	2.92	97							
Iodine	4	1 min.	Benzil[b]	2.95	98							
Benzoyl chloride	6	2 min.	Stilbenedibenzoate[c]	4.85	80	Bz + lig.	Prisms	158				
Acetic anhydride	5	15 min.	Stilbenediacetate[c]	3.5	82	Bz + lig.	Prisms	118				
p-Toluyl chloride	6	2 min.	Stilbenedi-*p*-toluate[d]	3.2	50	Bz	Prisms	199.5	80.3	5.3	80.6	5.4
Methyl iodide	6	4 hrs.	Stilbenedimethyl ether[e]	1.55	45	Bz + lig.	Needles	66–67	80.0	6.7	80.9	6.4
Allyl bromide	5	3 min.	Stilbenediallyl ether[f]	3.5	84	Bz + lig.	Needles	92–93	82.2	6.8	81.6	6.7
Triphenylchloromethane	8	1 hr.	Benzil[b,g]	2.7	90							
Sulfur	1.2	2 hrs.	Benzil[b]	2.7	90							
Chloroethylcarbonate	4.5	15 min.	Diethylstilbenedicarbonate	2.7	53	Alc.	Needles	69–70	67.4	5.6	67.1	5.5

[a] Hydrolysis of the disodium derivatives of anisil, 4,4′-diphenylbenzil and of α-naphthil gave 90, 98 and 80% yields, respectively, of the corresponding benzoins.

[b] During the reaction the violet colored complex was visible as an intermediate; the color changes in the reaction were the reverse of those engendered in the reaction between benzil and amalgam.

[c] These esters were identical with those obtained by Staudinger and Binkert from the dipotassium compound and by Gomberg and Bachmann from the iodomagnesium derivative of benzil.

[d] An 81% yield of a mixture presumably of the two possible stereoisomers was obtained; by repeated recrystallizations one of the forms was obtained pure. The ester is little soluble in alcohol or ligroin.

[e] The stilbenedimethyl ether is soluble in alcohol, very soluble in benzene and slightly soluble in ligroin. Staudinger and Binkert reported 127° for the melting point of a dimethyl ether which they obtained by interaction of benzil-dipotassium and dimethyl sulfate; they did not analyze their product.

[f] Soluble in hot alcohol; very soluble in hot acetone.

[g] The hydrolyzed mixture was treated with air in order to oxidize the triphenylmethyl; 6 g. of triphenylmethyl peroxide was obtained.

Experimental

In most of the reactions a 3-g. sample of benzil was shaken with 35 g. of 2% sodium amalgam in a mixture of 25 cc. of anhydrous ether and 25 cc. of dry benzene in a 60-cc. flask, the space above the mixture being filled with nitrogen. After a minute of shaking a violet colored solid was formed; this was usually converted to the orange colored precipitate of benzil-disodium in three to five hours. The benzil-disodium is practically insoluble in the solvent, for the supernatant liquid is colorless. During the addition of the reagent employed for reaction the mixture was cooled; all of the reactions were carried out at or below room temperature. In Table I are given the essential conditions and the principal products of the reaction; in most cases the end of the reaction was indicated by the complete disappearance of color from the mixture, which usually occurred in a shorter time than that indicated in the table. Although the derivatives of dihydroxystilbene are capable of existing in two geometrical isomers only one form was isolated in a pure state in each case.

Reaction with Carbon Dioxide.—When dry carbon dioxide was passed through the orange suspension of benzil-disodium from 5 g. of benzil, the color soon disappeared and a thick nearly colorless suspension of the sodium salt of stilbenedicarbonic acid was obtained; during the reaction some heat was evolved. Addition of water gave 4.75 g. of benzoin.

Reaction with Oxygen.—When dry air was passed through a suspension of benzil-disodium, the orange color changed to brown and after three hours the mixture was colorless; addition of water yielded 4.7 g. of benzoic acid and 1.0 g. of benzilic acid. Staudinger and Binkert obtained a similar mixture by oxidation of benzil-dipotassium at room temperature.

Reaction with Benzaldehyde.—Five cc. of benzaldehyde was added to the benzil-disodium from 3.0 g. of benzil. After the mixture had stood at room temperature for twenty hours it was poured into water; 2.2 g. of benzoin and 4.6 g. of benzyl benzoate were isolated.

Summary

Benzil-disodium, $C_6H_5C(ONa){=}(NaO)CC_6H_5$, is formed in quantitative yield by the action of 2% sodium amalgam on benzil in a mixture of ether and benzene at room temperature. Anisil, 4,4′-diphenylbenzil and α-naphthil yield disodium derivatives under similar conditions. This reaction offers a convenient method of obtaining these compounds and from them derivatives of dihydroxystilbene, $C_6H_5C(OH){=}(HO)CC_6H_5$.

ANN ARBOR, MICHIGAN RECEIVED JANUARY 8, 1934

[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF THE STATE UNIVERSITY OF IOWA]

The Preparation of Dibromoamine and its Reaction with Grignard Reagents

BY GEORGE H. COLEMAN, CHARLES B. YAGER AND HAROLD SOROOS

Monobromoamine[1] has been prepared in this Laboratory by a modification of the method of Moldenhauer and Burger.[2] The first attempts to adapt the method to the preparation of ethereal solutions of monobromoamine led to products in which the bromine to nitrogen ratio was considerably greater than 1.0. This suggested the possibility that dibromoamine was also formed. The formation of the two compounds can be represented by the equations

$$2NH_3 + Br_2 \longrightarrow NH_2Br + NH_4Br \qquad (1)$$

$$3NH_3 + 2Br_2 \longrightarrow NHBr_2 + 2NH_4Br \qquad (2)$$

By changing the manner in which the bromine and ammonia were brought together from that used in the preparation of monobromoamine and by changing the relative quantities used, ethereal solutions of dibromoamine have been prepared in which the bromine to nitrogen ratio was approximately 2.0. That the 2.0 ratio is not due to a mixture of monobromoamine and bromine is shown by the following considerations. The amber color of the solution of dibromoamine is distinctly different from the color of a solution containing enough free bromine to produce a ratio of bromine to nitrogen of 2.0. When ammonia is passed into a cold dibromoamine solution, no precipitate of ammonium bromide is formed. Such a precipitate would be formed immediately if free bromine were present.

Both monobromoamine and dibromoamine are unstable at 0° and are best prepared at temperatures obtainable with solid carbon dioxide. The rates of decomposition of the two compounds in ethereal solution at 0 and −72° are shown in Fig. 1. Dibromoamine is less stable at 0° than monobromoamine but rather anomalously can be prepared in greater concentration than monobromoamine. In Fig. 2 are shown the rates of decomposition of dibromoamine at 0 and −72° in ethereal solution of the higher concentration usually obtained. Attempts to prepare monobromoamine solutions of this concentration were not successful.

The reaction of dibromoamine was studied with nine Grignard reagents which were also used with monobromoamine. The results are given in Table I.

TABLE I

PERCENTAGE YIELDS OF AMINES, AMMONIA AND NITROGEN FROM DIBROMOAMINE AND GRIGNARD REAGENTS

Reagents	RNH_2	R_2NH	NH_3	N_2	Total
n-C_4H_9—Mg—Cl	15	5	70	7	97
n-C_4H_9—Mg—Br	5	1	89	..	95
n-C_4H_9—Mg—I	2	0.4	95	1	98
s-C_4H_9—Mg—Cl	21	5	62	8	96
t-C_4H_9—Mg—Cl	24	5	53	9	91
t-C_4H_9—Mg—Br	16	5	67	4	92
t-C_4H_9—Mg—I	3	1	89	7	100
C_6H_5—CH_2—Mg—Cl	34	6	41	4	85
$C_6H_5C_2H_4$—Mg—Cl	18	3	73	1	95

The percentage yields are calculated on the basis of the nitrogen content of the dibromoamine solutions. An excess of the Grignard reagent was always used. The reactions may be represented by equations similar to those given for the reaction of monobromoamine[1] with Grignard reagents. The yields of primary amines are less than those obtained with monobromoamine. The yields of secondary amines are much less than the yields of primary amines, a result which might be expected from a consideration of the reaction of alkyldichloroamines[3] with Grignard reagents. The variation in yields of amines with reagents prepared from chlorides, bromides and iodides which is characteristic of monochloroamine and monobromoamine was observed in this work.

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(1) Coleman, Soroos and Yager, THIS JOURNAL, **55**, 2075 (1933).

(2) Moldenhauer and Burger, *Ber.*, **62**, 1615 (1929).

(3) Coleman, THIS JOURNAL, **55**, 3001 (1933).